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INFLUENCE OF SOME FACTORS UPON HYDRIDING AND VARIATION OF PROPERTIES OF ZIRCONIUM ALLOY WITH I % Nb USED FOR FUEL ELEMENT CLADDING IN WATER - MODERATED WATER-COOLED POWER REACTORS

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I. Introduction

In recent years the scientists of many countries pay considerable attention to the problems of zirconium corrosion and hydriding.

The basic problem to be solved is determination of service life of zirconium alloy claddings of fuel elements and pipes operating under pressure in water-moderated water-cooled power reactors. There are many publications on this problem (I - 9).

These publications contain a lot of interesting experimental data and some theoretical concepts relating to the influence of numerous factors, such as chemical and phase composition of alloys, temperature of test, extent of irradiation, and others, upon kinetics of oxidation and hydriding resulting in variation of zirconium alloy properties.

These investigations along with the experience in operation of reactors have considerably extended our knowledge about the service life of the zirconium alloys. At the same time it should be emphasized that the problem of the service life of the zirconium alloys employed in power reactors has not been solved yet. In this connection, it is worth while mentioning the paper published in I963 (9) concerning the effect of stresses upon distribution of the precipitated zirconium hydrides. We consider this factor to be very significant but it should be noted that this aspect of zirconium alloy durability has not been sufficiently studied.

The present paper contains some results of experimental studies devoted to the effect of preliminary hydriding and subsequent irradiation upon the mechanical properties and microstructure of specimens and fuel element claddings made of zirconium alloy with I % Nb; the data are cited concerning the influence of the amount of stresses upon orientation of hydrides in zirconium alloys with I and 2.5 % Nb.

II. Influence of Preliminary Hydriding Upon Mechanical Properties and Corrosion Behaviour Of Zirconium Alloys With I % Nb

To determine the influence of hydrogen upon mechanical properties of the zirconium alloy, the specimens were hydrided by means of gas saturation in the apparatus described earlier (8) at 600°C and then slowly cooled at the rate of 4°/ min.

The typical structures of the alloy after hydriding are presented in Fig.I. Hydriding of the alloy in the ustressed condition was accompanied by formation of hydride stringers located as a rule in random or sometimes in the direction of the previous deformation.

Initially the alloy contained 0.002 wt % H[x]. The specimens were hydrided to the various hydrogen contents. The specimens were irradiated in the Reactor for Physical and Technical Investigations in water loop (water temperature of 290°C, pressure of I00 atm) for 4000 hours till the integrated flux of $I.5 \cdot I0^{20}$ n/cm^2 [xx] was obtained; in dry channel at I30°C-till the integrated flux of $3.5 \cdot I0^{20}$ n/cm^2 was obtained. Simultaneously the control specimens were examined in the non-irradiated portion of the water loop circuit at the same parameters of water for 4000 hours.

The results of the tensile tests are presented in Fig.2.

The test results show that with the increase of hydrogen content up to 0,08% the ultimate strength and yield point[xxx] of the non-irradiated specimens increase the most considerably, and the relative

x) Here and below hydrogen contents are indicated in per cents by weight.

xx) Here and below the integrated fluxes are given for the neutrons whose energy exceeds I Mev.

xxx) 0,2% offset.

elongation of the specimens mostly drops at the same content of hydrogen. The same phenomena are observed in the non-irradiated specimens held in water flow (290°C and I00 atm) for 4000 hours. (curves 2). Irradiation increses the ultimate strength and yield point and reduces the relative elongation for all the specimens. In this case the effect of the hydrogen content diminishes.

The tensile tests of the irradiated specimens at 350°C showed that the ultimate strength increases by 50%, and the relative elongation decreases up to II%. More over, hydrogen contents have a little effect both on tensile strength, and relative elongation.

This may be explained, on one hand, by decrease of strength caused by high temperature and, on the other hand, by transition of hydrogen into solid solution.

Sensitivity of the alloy to stress concentration may be easily determined by notch-tensile tests.

Fig.3 shows the dependence of the notch-tensile strength (σ_{bn}) to unnotched-tensile strength (σ_b) ratio on hydrogen content in the alloy before and after irradiation. As it may be seen, the σ_{bn}/σ_b ratio decreases with increase of hydrogen content in the non-irradiated alloy. However, it is more than 1.0 all over the range of hydrogen contents. This proves that under the given test conditions normal stresses are less than cleavage strength. In case of irradiated specimens the σ_{bn}/σ_b ratio is reduced more considerably and reaches 1.0 at the hydrogen content of 0.07%. With increase of integrated irradiation flux the notch sensitivity of the alloy will grow up and the σ_{bn}/σ_b ratio equal to 1.0 will be obtained at lower content of hydrogen in the alloy. Thus, the notch sensitivity of the alloy is a function both of the hydrogen content and irradiation conditions.

For the impact toughness tests the specimens of 5 mm diameter with the notch I mm deep and notch root radius = 0,25 mm were used. In this case the impact toughness values are 3-4 times less than those obtained with Mesnager test pieces.

The results of the impact tests of the unhydrided specimens and specimens preliminary hydrided up to 0.04 and 0.I % H are shown in fig.4. Irradiation was performed in "dry" channel at I30°C by the integrated flux of $3 \times 10^{20} n/cm^2$.

With increase of test temperature from -80° to +300°C impact toughness of the non-irradiated specimens with initial hydrogen content of 0.002% rises from 2 to 5 kgm/cm^2. Preliminary hydriding to 0.04 % H decreases impact toughness from 5.5 and 2 kgm/cm^2 in initial specimens to 2.5 and I kgm/cm^2, respectively. Increase of hydrogen content up to 0.I % still more reduces resistance of the alloy to impact loads.

Irradiation of the alloy with initial content of hydrogen results in reduction of impact toughness by 20-30 %. In this case transition from ductile to brittle state of the alloy is clearly pronounced. At the hydrogen content of 0.04 and 0.I % irradiation of the alloy under the specified conditions brought to further deterioration of its impact properties (at the test temperatures up to 300°C impact toughness comprises 0.5 - I.5 kgm/cm^2).

Summarizing all the experimental data cited above, a conclusion can be drawn that at irradiation up to I0^{20}n/cm^2 and at temperatures ranging from 20 to 350°C the hydrogen content up to 0.04 % exerts a negligible effect upon the static mechanical properties of a zirconium alloy with I % Nb. Such a content of hydrogen considerably reduces impact toughness at temperatures below 200°C. Furthe increase of hydrogen content at the same dose of irradiation considerably impairs the properties which are responsible for structural strength and reliability of the alloy.

Specimens of zirconium alloy with I % Nb containing from 0.002 to 0.I % H were tested for corrosion in the circuit of the water loop in the RPT under the following conditions: water temperature 290°C, pressure I00 atm, rate of flow 4.5 m/sec. The specimens were located both in the active portion of the circuit where they were irradiated with the integrated dose of I.5·I0^{20}n/cm^2 and in the inactive portion of the circuit. The total time of test under these parameters was 4000 hours. Considerable increase (~ 8 times as large) of oxidation of irradiated specimens with 0.002 % hydrogen content should be noted. At the hydrogen content of 0.02 % and more there is no conside-

342

rable difference between weight gains of the irradiated and non-irradiated specimens. With increase of hydrogen content a certain decrease in weight gains is traced. This may be supposed to be connected with deterioration of oxide film adhesion which results in extensive washdown of the oxide film due to errosion by the water stream.

Tests in static autoclaves with water temperature of 350°C and pressure of 168 atm carried out for 4000 hours proved that preliminary hydriding did not effect the amount of weight gains.

III. Study Of Test Fuel Elements With Claddings Made Of Zirconium Alloy With 1 % Nb.

A test cluster of fuel elements with claddings of zirconium alloy with 1 % Nb was placed into the water loop of the RPT. The fuel element claddings were preliminary hydrided to 0.01, 0.02, 0.03, 0.04 and 0.05 % of hydrogen content. The fuel element diameter was 10.2 mm and length, 200 mm. The cluster of fuel elements with pellets of uranium dioxide has successfully operated for 4000 hours in water under a pressure of 100 atm and at cladding surface temperature of 300°C. The thermal load amounted to 520 W/cm, integrated flux was $1.5 \cdot 10^{20}$ n/cm^2.

After testing in the autoclave, samples for metallographic studies and ring-shaped specimens for determination of mechanical properties were cut out of the claddings. The metallographic study of the fuel element claddings proved that samples cut out of various zones of a single element possess identical microstructure. Comparing the obtained microstructures

342

with the initial one we can, however, see the change of hydride type and arrangement in the claddings tested in the reactor. Before irradiation (fig. 1.) the hydrides in the cladding microstructures had the shape of long dark stingers preferentially oriented along circumference and uniformly distributed over the cladding cross-sections. The amount of hydrides increased with increase of hydrogen content. After test in the reactor refining the hydrides occure and their distribution changed (fig. 5). As it is clearly seen on the microphotographs, the most of the hydrides displaced towards the outer less heated portion of the claddings.

The mechanical properties of claddings were checked on the ring-shaped specimens, 2.5-3.0 mm deep. These specimens were subjected to transverse tension in a special device.

The mechanical properties of the non-irradiated ring-shaped specimens cut out of pipes containing from 0.002 to 0.06 % of hydrogen are following: ultimate strength - 28-35 kg/mm^2 and relative elongation - from 12 to 17 %.

The tensile strength of ring-shaped specimens cut out of the fuel element cladding operated in the water loop of the RPT increase by 45-85 % as compared to that of the non-irradiated ring-shaped specimens. With increase of hydrogen content from 0.002 t0 0.06 % H the ultimate strength of the alloy is reduced from 53 to 47 kg/mm^2. This reduction in strength is the result of excessive sensitivity of the irradiated alloy

342

with high content of hydrogen to stress concentration.

The values of cleavage strength and their spread seem to be determined by heterogeneity of alloy structure possessing brittle hydride inclusions which serve as stress raisers. The relative elongation after irradiation decreases and ranges from 8 to 3 % depending on the hydrogen content. It should be noted that certain number of specimens failed with zero elongation.

The analysis of the test data proves that presence of highly hydrided surface layer is a determinant of the cladding ductility and load-carrying capacity.

IV. Studying Nature Of Hydriding Under Stress Of Zirconium Alloys With 1 and 2.5 % Nb.

The studies were carried out on pipes (with outer diameter of 10.2 mm, inner diameter of 8.8 mm and length of 120 mm) made of zirconium alloys with 1 and 2.5 % Nb. The pipes were filled with the required quantity of water, sealed by argon-arc welding, and then were placed into autoclaves with water the quantity of which was quite enough to ensure the outside steam pressure of 100 atm at 400°C. The amount of water poured inside the pipe was so selected as to ensure various excessive internal pressure at the temperature of 400°C and thus to build up the specified tensile stresses in the pipes.

In the course of tests, the pipe outer diameters were measured to determine the phenomena of creep in the transverse

342

direction. The rate of creep of the alloy with 1 % Nb comprised 3.10^{-4}%/hr for 450-1000 hours. The rate of creep of the alloy with 2.5 % Nb comprised $2.4 \cdot 10^{-4}$ %/hr for 1500-- 2000 hours. The microstructures of these pipes are presented in fig. 6. In the case of two-side contact of the water steam with the pipe walls subjected to tensile stresses ranged from 1.5 kg/mm^2 to 11.8 kg/mm^2, the hydriding of the pipe walls with different orientation of precipitated hydrides took place. It is worth while mentioning that at stresses up to 3.0 kg/mm^2 hydride stringers concentrically arranged were formed in the pipes made of zirconium alloy with 1 % Nb. At stresses of 4.4 kg/mm^2 and over the stringers of hydrides were arranged in radial direction. With increase of stresses the extention of the radial hydrides in the pipe cross-sections progressively increased. In pipes made of stronger zirconium alloy with 2.5 % Nb the radially oriented hydrides were formed at the stress of 8.8 kg/cm^2 and over. For both alloys the critical stresses at which radially oriented hydrides are formed range within 0.4-0.5 of the yield strength of each alloy at the test temperature.

In accordance with spectographic analysis results, the content of hydrogen in the zirconium alloy with 1 % Nb irrespective of imposed stresses was of the order of 0.01 % after 1000 hour testing, and that of the zirconium alloy with 2.5 % Nb, 0.02 % after 2000 hour testing.

Though the absolute quantity of hydrogen absorbed by pipes made of both alloys was actually the same (irrespective of imposed stresses), the influence of the hydrogen content upon

342

the mechanical properties of the ring-shaped specimens was different due to various orientation of the hydrides. The results of tensile tests of the ring-shaped specimens cut out of pipes made of zirconium alloy with 1 % Nb after having been corroded in steam at a temperature of 400°C are presented in fig. 7. The curves show that pipes subjected to stresses of 1.5 and 3.0 kg/mm^2 retained their initial values of elongation and strength nearly unchanged. At stresses ranging from 5.8 kg/mm^2 to 11.8 kg/mm^2 the relative elongation was reduced by 50 % and 80 % respectively and the ultimate strength decreased to 28 kg/mm^2. This reduction in ductility and strength is explained by structural piculiarities of hydride arrangement in the pipe cross-sections.

The similar test was carried out on pipes made of zirconium alloy with 1 % Nb which were hydrided at the hydrogen temperature of 500°C and at the pressure of 600 mm Hg. The tensile stress in the pipe wall during hydriding was equal to 2.5 kg/mm^2. The specimen was allowed to absorb the required quantity of hydrogen (to ensure hydrogen content of 0.02 %) for 3-5 min at a temperature of 500°. After hydriding, the specimen was held for 3 hours (without hydrogen) and then was cooled at a rate of 4°/sec. At the metallographic examination radially oriented hydrides extending from the surface to certain depth, can be clearly seen.

The stress of 2.5 kg/mm^2 comprises 0.4-0.5 of this alloy yield point at the 500°C.

342

These tests prove that formation of radially oriented hydrides is a function of values of the tensile stress and does not depend upon the methods of hydriding. Even at the hydrogen content of 0.01 % with radially oriented hydrides the pipe properties are sharply impaired; that proves the paramount importance of the values of tensile stress when using zirconium alloys in water-moderated water-cooled power reactors. On all other conditions being equal, preference should be given to the zirconium alloys possessing high yield point as in this case the value of the allowable hydriding stress will be higher and reliability of operation will correspondingly increase.

The allowable hydriding stress of the alloy is the maximum tensile stress at which radial orientation of the hydrides under the specified service conditions does not yet occur. Evidently, it is to be taken into account along with other parameters in designing zirconium alloy claddings for fuel elements or zirconium alloy pipes for service under pressure.

V. Metallographic Study Of Different Rod-Type Fuel Element Clusters.

The state of the material of fuel element claddings tested in the reactor was metallographically examined. The list of fuel element clusters together with service conditions in the reactor are given in table 1. The metallographic examinations were performed both on the clusters which successfully passes t[illegible]ch failed. In both cases hydriding of the claddings was observed in more of less extent. Fig. 8 shows the microstructures of claddings of the clusters Nos 1 and 2. The microphotographs show that the hydrides are arranged both on the circumference and radially in the form of small dark stringers. In both clusters the fuel element claddings failed during tests in the reactor. Fig. 8-3 shows that in the zone of fracture the hydrides are oriented radially. The claddings of clusters Nos 3 and 4 contain a very negligible amount of hydrides. The microstructures of claddings of cluster No 5 are shown in fig. 9.

Fig. 10. shows the microstructures of the samples out out of one of the fuel element clusters of the first charge of the "LENIN" ice-breaker reactor. The microphotographs reveal presence of hydride phase in some areas of the claddings. The ring-shaped specimens cut out of the fuel element claddings were subjected to mechanical tests which proved that their strength increased by 40 % and the relative elongation decreased by 60 % as compared to the non-irradiated specimens. This means that even after operation in the reactor for 3 years the fuel element can remain serviceable.

VI. Conclusion.

Numerous experimental data published now in many countries on corrosion and hydriding of zirconium alloys, a lot of water loop tests carried out, and extensive experience in the field of employment of fuel elements with zirconium alloy claddings

342

in power reactor prove that in certain conditions these alloys possess high operational reliability. At the same time the behaviour of zirconium alloys was not satisfactory in some cases. Many causes of these failures have been already revealed. However we suppose that up to recent time the effect of stresses on the hydriding processes was studied very little and therefore was not taken into account in practice properly. Now it is clear that this factor effects to a certain extent on the operational reliability of the zirconium alloys, therefore firstly this problem must be studied more thoroughly and, secondly, this factor should be strictly taken into consideration while designing reactors.

Table 1.

Test Conditions Of Clusters Of Rod - Type Fuel Elements With Claddings Of Zr + 1 % Nb Alloy

Cluster No.	Test conditions				
	Cladding surface temperature, ^{o}C	Thermal load, W/cm	Time of test, h	Burn-out, mg.W.d/t	Neutron flux x) $\times 10^{20}$
1.	310	297	3600	7000	1.3
2.	320	297	6900	13400	2.5
3.	350	164	9900	45000	5.3
4.	300	186	13500	20000	3.4
5.	300	520	6300	1400	2.3

x) Fast neutron flux comprises 30 % of the thermal neutron flux.

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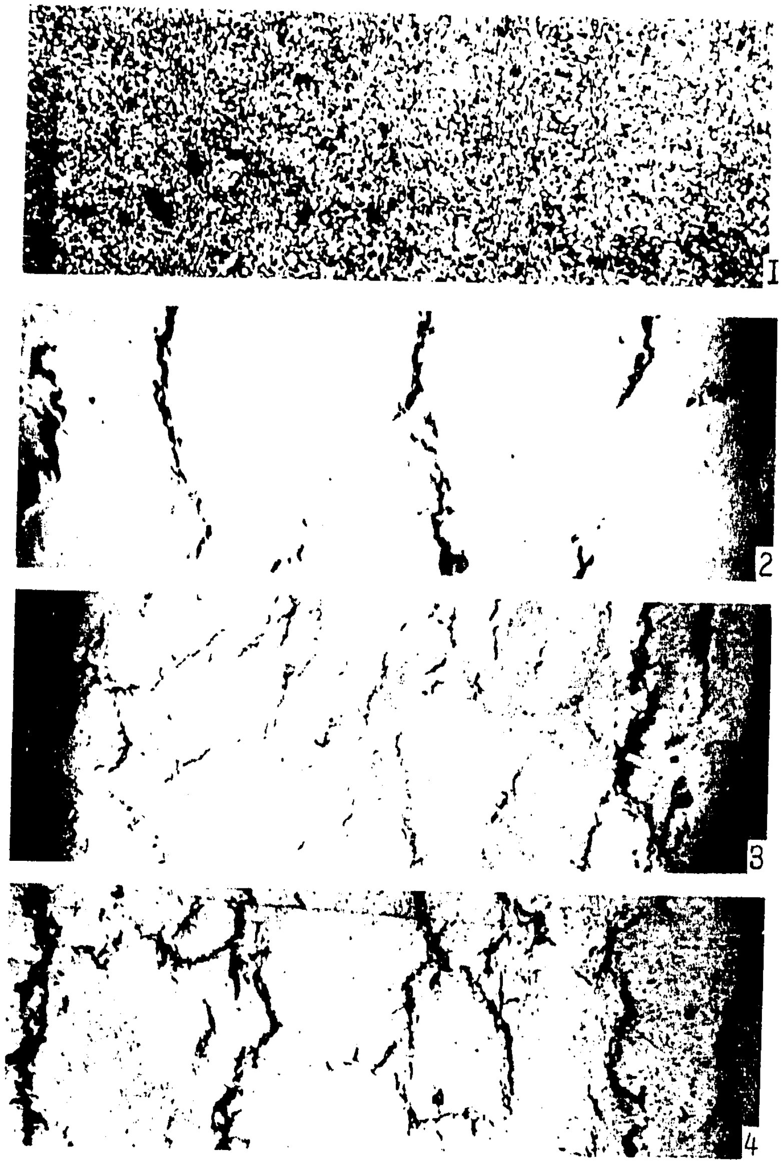

Fig. 1. Microstructures of pipes with various content of hydrogen in alloy before irradiation. x 200.

1. Initial state (annealing at 700°C for 30 min) - - 0.002 % H.
2. Alloy with 0.02 % H.
3. Alloy with 0.04 % H.
4. Alloy with 0.06 % H.

342

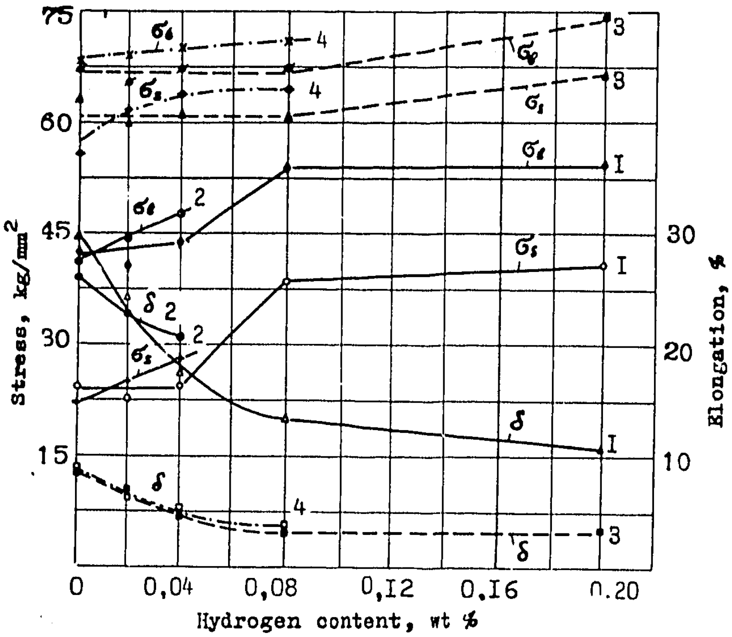

Fig. 2. Influence of hydriding and irradiation on alloy strength and ductility. Temperature of test 20°C.

1. non-irradiated.
2. non-irradiated held in water at 290°C for 4000 hours.
3. irradiated by the flux of $3.5x10^{20}$n/cm², 130°C.
4. irradiated by the flux of $1.5x10^{20}$n/cm², 290°C.

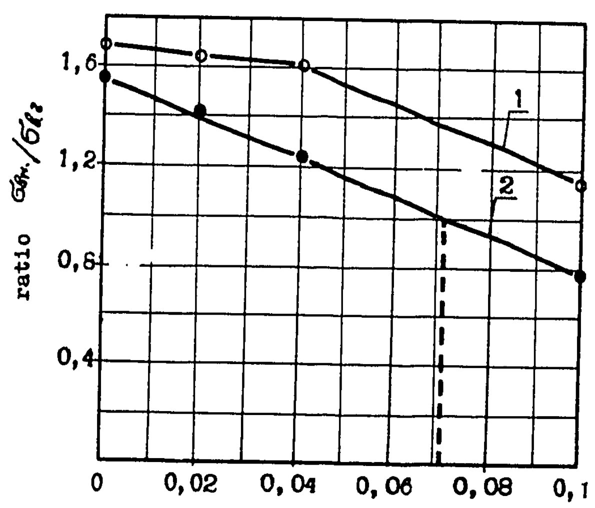

Fig. 3. Influence of hydriding on notch-tensile strength/tensile strength ratio $\frac{\sigma_{\theta н.}}{\sigma_{\theta з.}}$

1. non-irradiated
2. irradiated with dose of $5x10^{19}$n/cm², at 135°C.

342

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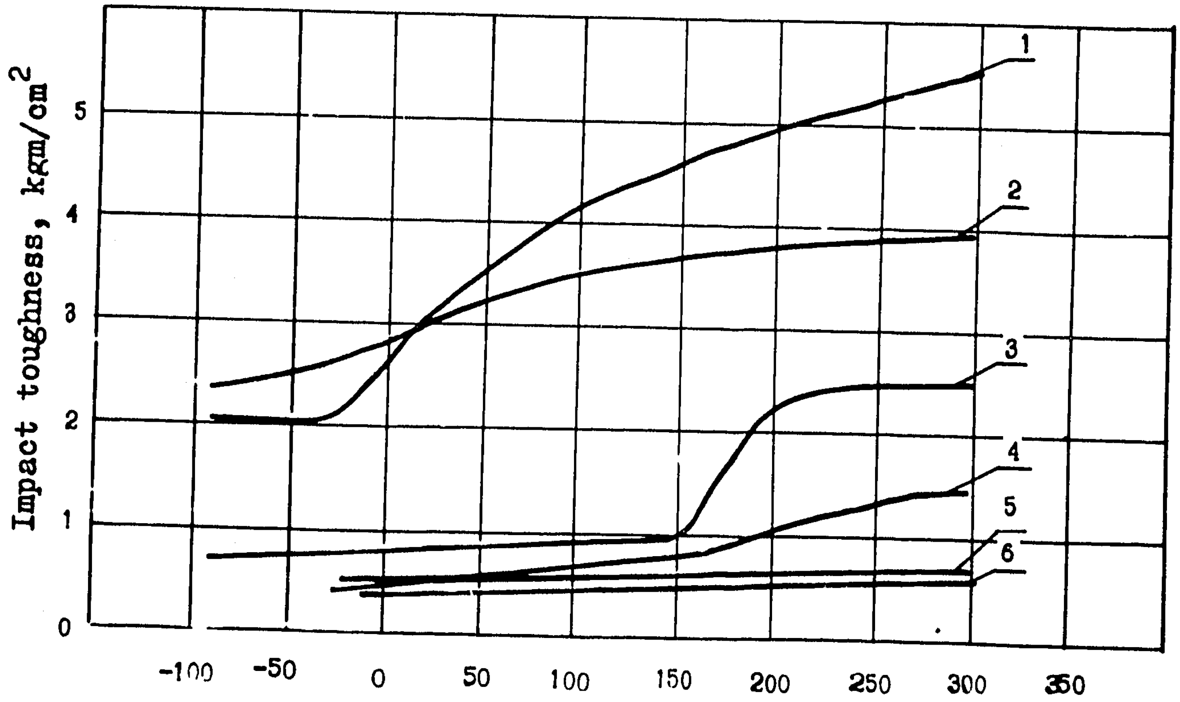

Fig. 4. Effect of the test temperature upon impact properties of the alloy. The specimens were irradiated by flux of $3.0 \times 10^{20} n/cm^2$, at 125°C.

1. Alloy with the initial hydrogen content	1) before irradiation
	2) after irradiation
2. Alloy with 0.04% H	3) before irradiation
	4) after irradiation
3. Alloy with 0.1 % H	5) before irradiation
	6) after irradiation

342

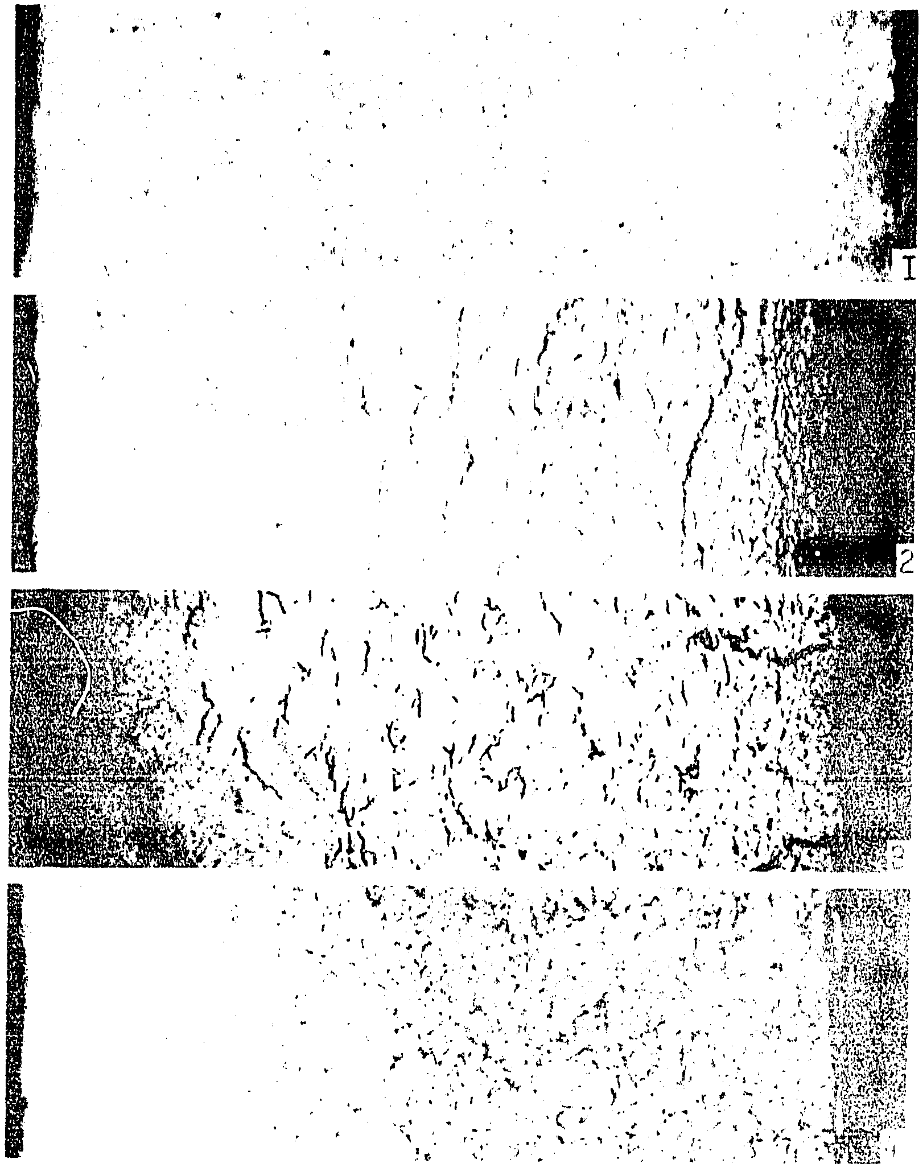

Fig. 5. Microstructure of fuel element claddings after operation in reactor. x 200.

Right—the outer surface of the cladding.

1. Alloy with 0.002 wt.% H.
2. 0.02 wt. % H.
3. 0.04 wt. % H.
4. 0.06 wt. % H.

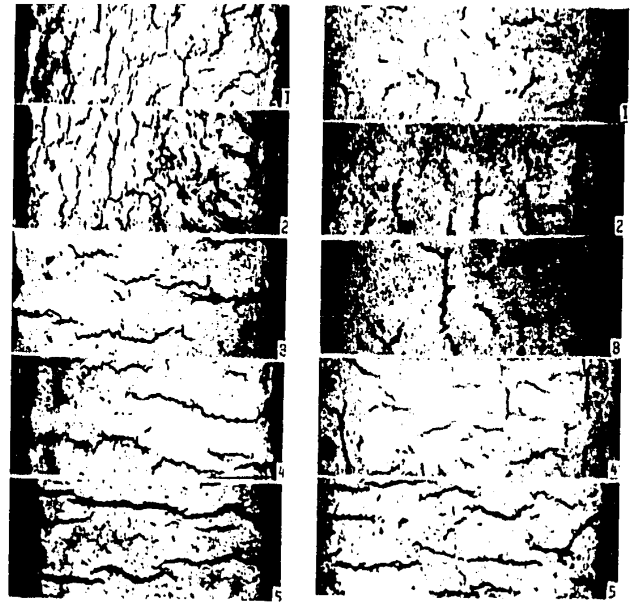

Fig. 6. Microstructures of pipes made of zirconium alloy with 1 % Nb after testing them in steam at 400°C, for 1000 hours and those of the alloy with 2.5% Nb after testing in steam at 400°C for 2000 hours. x 115.
Right - the outer surface of the pipes.

Alloy with 1% Nb:	Alloy with 2.5% Nb:
1. stress of 1.5–1.0 x) kg/mm²	1. stress of 1,5–0.3 x) kg/mm²
2. stress of 3.0–2.4 kg/mm²	2. stress of 4.4–3.5 kg/mm²
3. stress of 4.4–3.9 kg/mm²	3. stress of 5.9–5.3 kg/mm²
4. stress of 5.9–5.5 kg/mm²	4. stress of 8.8–8.3 kg/mm²
5. stress of 11.8–11.0 kg/mm²	5. stress of 11.8–11.5 kg/mm²

x) Stress is reduced due to creep strain and due to water consumption for corrosion.

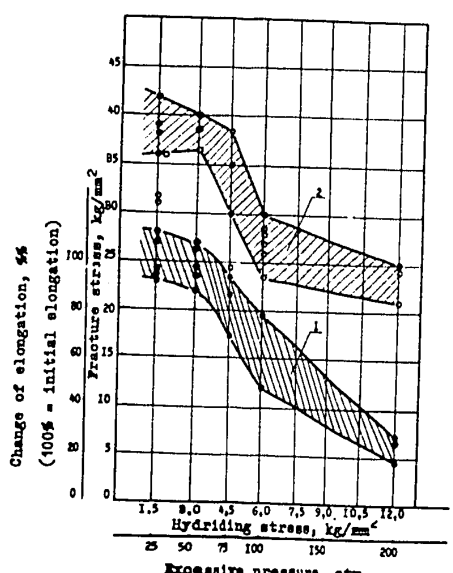

Fig 7. Influence of stress corrosion on mechanical properties of pipes made of zirconium alloy with 1% Nb which were tested for 1000 hours in steam at 400°C. (ring-shaped specimens were tested).

1. Change of elongation, %
2. Fracture stresses.

342

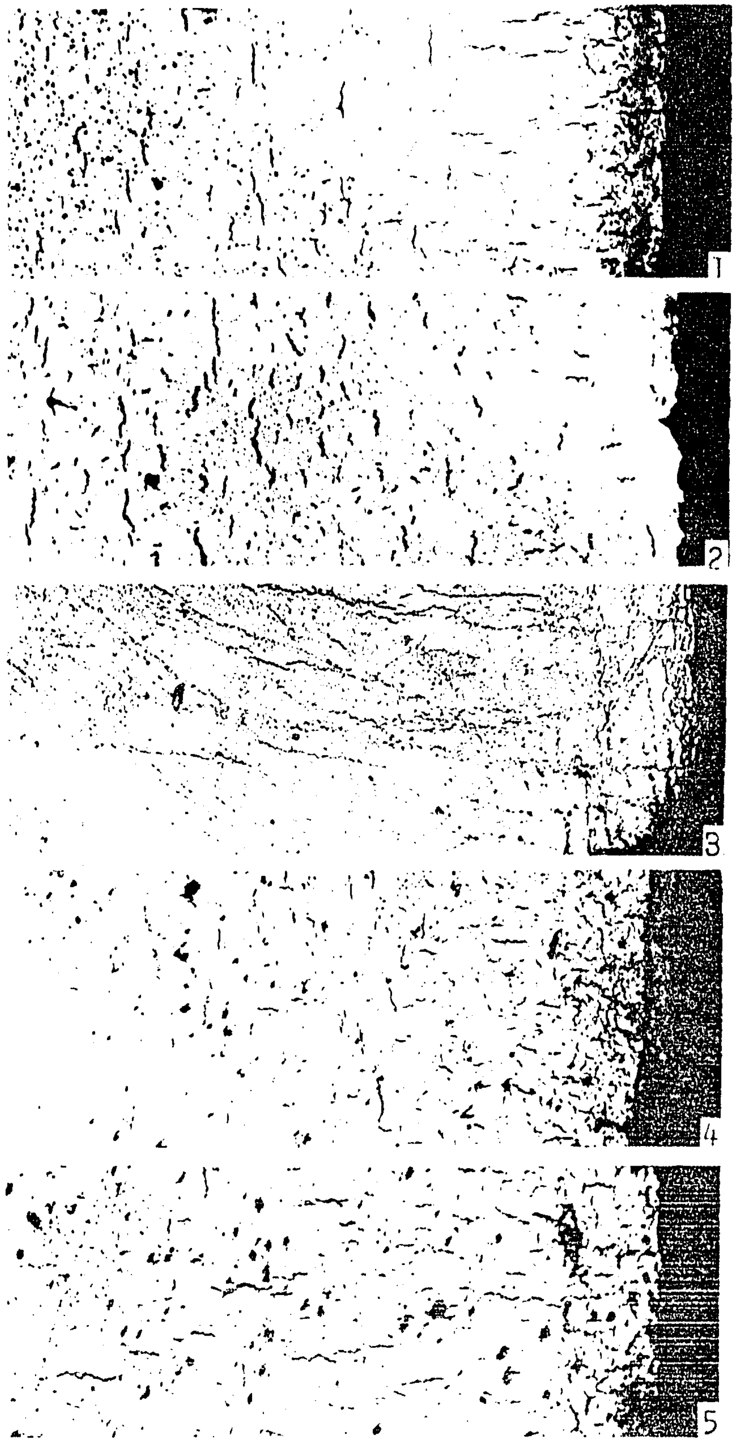

Fig. 8. Microstructures of fuel element claddings of cluster Nos 1 and 2. x 200.

Right - the outer surface of the cladding.

1, 2, 3 - cluster No. 1; 3 - zone of fracture;

4, 5 - cluster No. 2.

342

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342

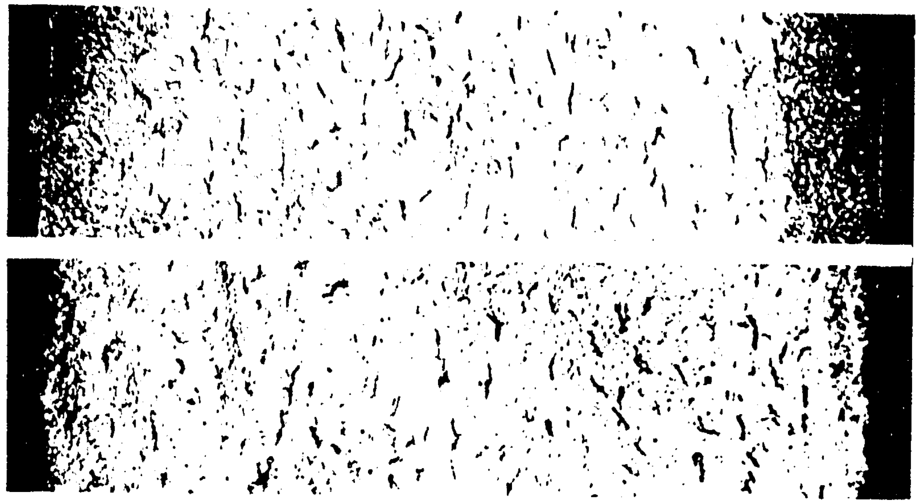

Fig. 9. Microstructures of fuel element claddings of cluster No. 5. x 200.
Right - the outer surface of the cladding.

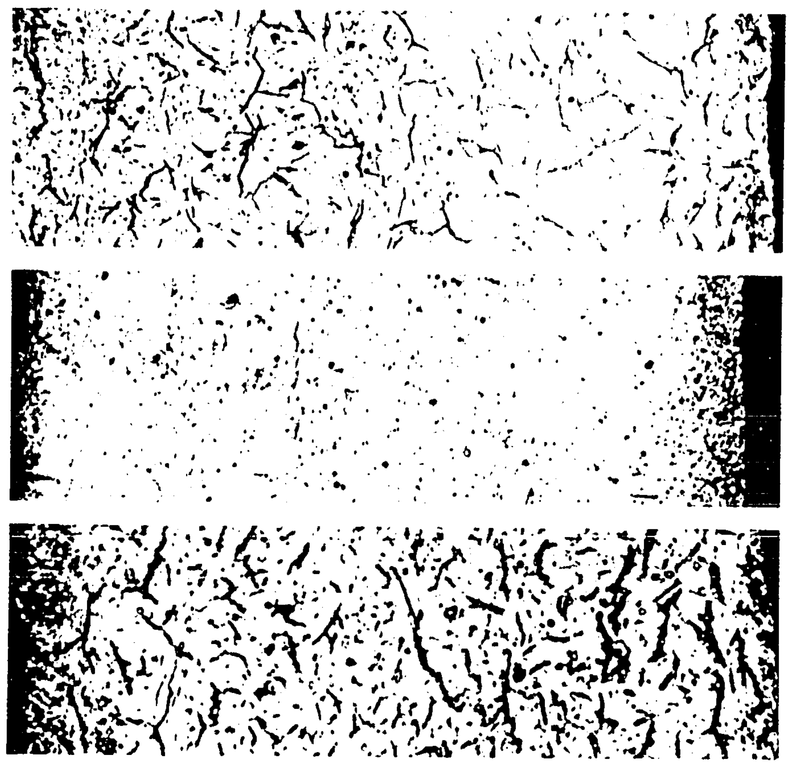

Fig. 10. Microstructure of fuel element cladding of one of channels of "LENIN" ice-breaker. x 200.
Right - the outer surface of the cladding.

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